A series of water soluble block copolymers have been synthesized by using RAFT and free radical polymerization technique. RAFT technique has been of great interest to researchers these days because of the predictable molecular weight, low PDI and controlled architectures with this technique. The RAFT process has proved to be of versatile nature in terms of selection of monomer and reaction conditions. Free radical polymerization (FRP) is facile technique to synthesize copolymers over the various types of vinylic monomers. FRP is most acceptable technique by industries and researcher globally. It is cheaper, faster, sensitive and productive synthesis process. The block copolymers synthesized in this work are smart polymers having stimuli-responsive behaviour and water soluble biodegradable nature. Responsive water-soluble polymers have been proposed as flocculants and have also been used in the work of bio-medical applications such as drug delivery. Current research on smart block copolymers is going on to make them biocompatible and non-toxic with controlled degradation rate. Some of the most commonly used smart polymers are, poly(N-isopropylacrylamide), 2(acrylamido)-2-methylpropanesulfonate, Poly(methacrylic acid) etc., used in these days and are of high interest. These materials are in the form of hydrogels, which are easy to synthesize and use. Hydrogels are three-dimensional polymer networks with hydrophilic polymer chains which are connected either by physical association or by chemical bonds. And able to absorb a large amount of water. Due to their high water content hydrogels can be used as biomaterials in medical applications. It can be used in drug-delivery system and agriculture if we can control its solute release over time.

Chapter one "Introduction"

In this chapter there is a brief introduction about water soluble polymers their monomers, smart copolymers, hydrogels and their application in flocculation, drug delivery, etc. It also highlights the objectives of the thesis.

Chapter two "Literature review"

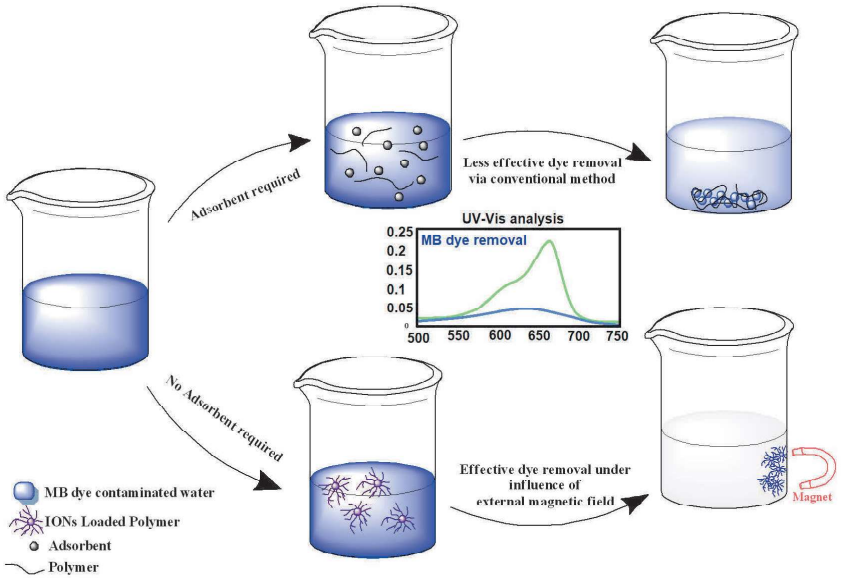
This chapter consists of review on water soluble polymers and their methods of synthesis. Different methods of polymerisation like free radical polymerisation, atom transfer radical polymerisation (ATRP) and reversible addition fragmentation transfer (RAFT) have been discussed. Then there is discussion on their applications in, wastewater treatment by

flocculation method and its mechanism, drug delivery and fertilizer release are discussed in this literature review.

Chapter three: "Synthesis of IONP's Decorated Graft Copolymers and Study of their Magnetic Force Induced Wastewater Treatment**"**.

Our work is focused on facile synthesis and modification of amylopectin grafted block copolymers by using reversible addition−fragmentation chain-transfer (RAFT) technique. This technique yield polymers with controlled molecular weight, low polydispersity indexes and is feasible with a wide range of monomers. Five different grades of amylopectin grafted polymethacrylic acid and polyacrylamide block copolymers, AP–g–(PMAA–b–PAM)–1 to AP–g–(PMAA–b–PAM)–5, have been synthesized via RAFT polymerization by employing amylopectin based macro chain transfer agent (AP–g–PMAA), and varying the amount of acrylamide. AP–g–(PMAA–b–PAMs) have been upgraded as smart responsive graft copolymers, AP–g–(PMAA–b–PAM)–I–1 to AP–g–(PMAA–b–PAM)–I–5, through the incorporation of Iron oxide (Fe_3O_4) nanoparticles (IONP's) via condensation reaction. The polymeric materials have application in suspended particles (Kaolin) and methylene blue dye removal (without any adsorbent) from contaminated water and has been extensively characterised by Energy Dispersive X-ray Analysis (EDAX), Fourier Transform Infrared Spectroscopy (FT-IR), Proton magnetic resonance spectroscopy (^{1}H-NMR), Scanning Electron Microscopy (SEM), Ultraviolet-visible spectroscopy (UV-VIS.), Gel Permeation Chromatography (GPC), Transmission Electron Microscopy (TEM), Thermogravimetric analysis (TGA) and X-ray Diffraction (XRD) analysis. AP–g–(PMAA–b–PAM)-Is have been used to remove methylene blue dye from water by applying external magnetic field. AP–g–(PMAA–b–PAMs) have been studied for removal of model contaminant (Kaolin) from

water. The upgraded block copolymers have shown best performance in wastewater treatment.

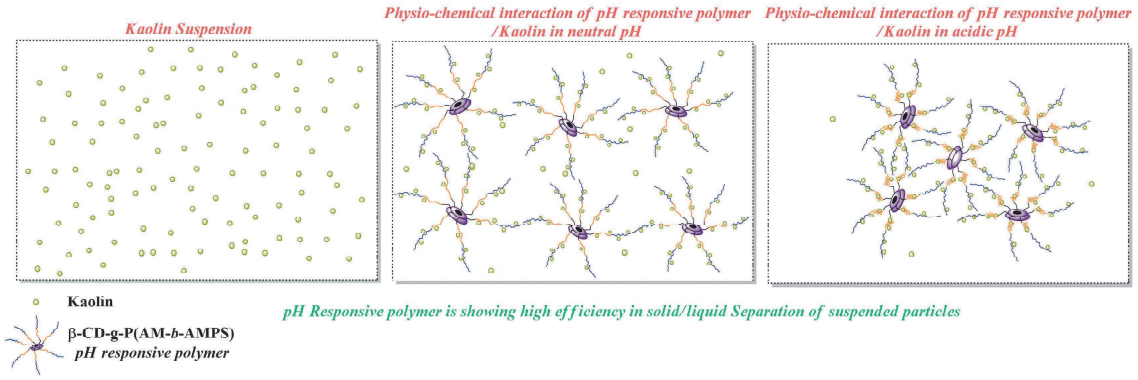


Scheme 1: Dye removal performance of IONP's Decorated Graft Copolymers with or without external magnetic field.

Chapter four: "pH Tempted Micellization of β-Cyclodextrin based Diblock Copolymer and its Application in Solid/Liquid Separation".

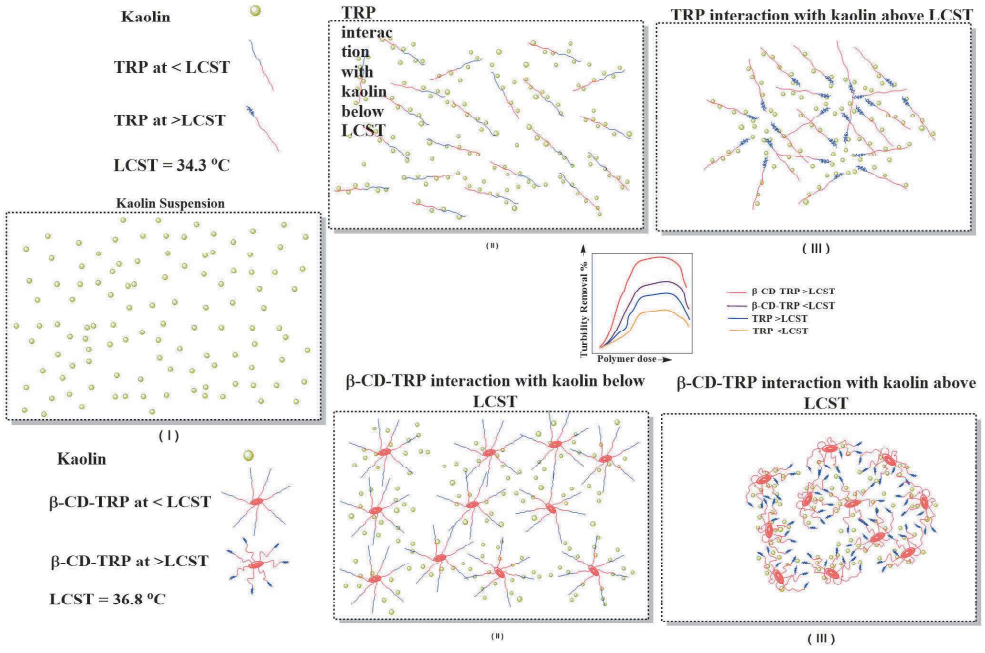
This work focuses on facile synthesis of pH responsive diblock copolymers based on acrylamide (AM) and 2-Acrylamido-2-methyl-1-propane sulfonic acid (AMPS) grafted on β-Cyclodextrin and have application in solid/liquid separation. β-CD based chain transfer agent (CTA) has been synthesized by one pot synthesis method. Three different grades of β-Cyclodextrin based Macro CTA were synthesized through RAFT polymerization technique. Macro CTA have been used further in synthesis of five different grades of β-CD grafted pH-responsive diblock copolymers i.e. (β-CD-PRP's) by varying the amount of AMPS. The polymeric materials were characterized by Fluorescence Spectroscopy, FT-IR, GPC, 1H-NMR, SEM, TEM, TGA, and XRD. β-CD-PRP's shows their micellization properties at acidic pH < 6.57 with polymer conc. > 0.336 mg/mL and has also been studied for removal

of model contaminant (kaolin). Among all grades of diblock copolymers, grade 3 shows best performance in the removal of kaolin from aqueous solution at 7 and 5 pH values.


Kaolin Suspension
Physio-chemical interaction of pH responsive polymer /Kaolin in neutral pH
Physio-chemical interaction of pH responsive polymer /Kaolin in acidic pH
Kaolin
β-CD-g-P(AM-b-AMPS)
pH responsive polymer
pH Responsive polymer is showing high efficiency in solid/liquid Separation of suspended particles

Scheme 2: Flocculation performance/physio-chemical interaction profile of pH responsive diblock copolymers over kaolin suspension in neutral and acidic medium.

Chapter five: "Synthesis, characterization and flocculation studies of β-Cyclodextrin based stimuli- responsive star copolymer: An Environmental remediation".

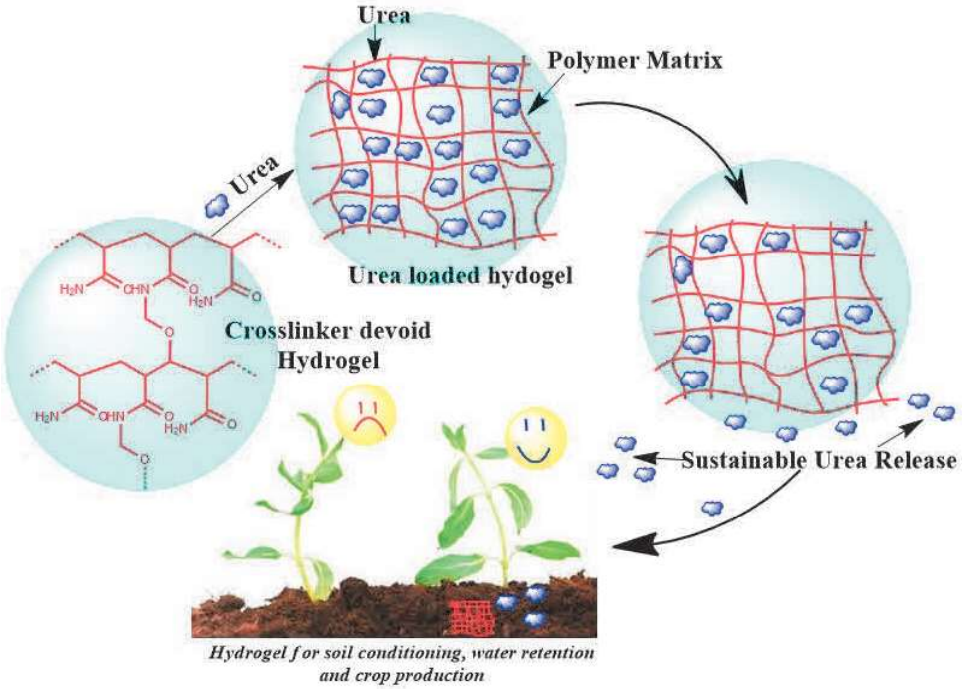


Scheme 3: Enhanced flocculation performance of TRP and β–CD-TRP (below and above LCST).

Thermo-responsive star polymers have been synthesized by using Poly(NIPAM-b-DMA) diblock copolymer and β-Cyclodextrin. The synthesis of thermo-responsive diblock copolymer (TRP) has been done by reversible addition-fragmentation chain transfer (RAFT) mediated aqueous polymerization using N-isopropylacrylamide and Di-methylacrylamide as monomers. Mercaptopropionic acid is used as in-situ CTA to synthesize PNIPAM i.e. macro CTA. The polymeric materials were characterized by FT-IR, GPC, ^{1}H-NMR, Particle Size Measurement, SEM, TGA, UV-visible spectroscopy and XRD. PNIPAM, TRP and β-CD-TRP shows LCST at 32.8^{o}C, 34.3^{o}C and 36.8^{o}C respectively. TRP and β-CD-TRP have also been studied for removal of model contaminant (kaolin). Among all grades β-CD-TRP 4 shows best performance in the removal of kaolin from aqueous solution at 25^{o}C and 50^{o}C.

Chapter six: "Synthesis of Cross-Linker Devoid Novel Hydrogels: Swelling behaviour and Controlled Urea Release Studies".

Hydrogel incorporated fertilizers are most challenging materials in agriculture industries, because of their soil conditioning properties and potential of sustainable release of fertilizer. Polyacrylamide based biocompatible, non-toxic and environmentally benign polymeric hydrogels were synthesized by using acrylamide (AM) and N-hydroxymethyl acrylamide (NHMA) as monomers and potassium persulfate (KPS) as an initiator. Further modification was carried out with incorporation of urea into the hydrogel at the time of synthesis. Eight different formulations of hydrogel without using any cross-linking agent were synthesized by varying the ratio of NHMA in first four grades and used fixed amount of urea in next four grades respectively. These grades were characterized by using FT-IR, SEM, TGA and XRD. In this article, the swelling properties and equilibrium swelling ratio were predicted at different pH and temperature. Also the release of urea from urea incorporated hydrogel was studied and analyzed through UV-Vis spectroscopy. Prediction of the possibility of using these hydrogels in agriculture fields is the main objective of this work.

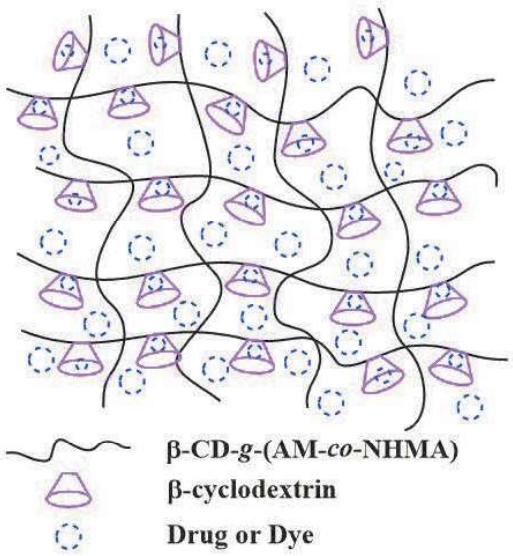


Scheme 4: Schematic representation of application of sustainable release of Urea from urea loaded hydrogel in agriculture.

Chapter seven: "Synthesis, Characterization of β-CD based Novel Hydrogels with Dual Idea of Drug Release and Dye Removal"

In our recent work we have reported crosslinker devoid hydrogels. After observing the successful swelling and water retention properties, we have introduced β-cyclodextrin in acrylamide-*co*-N-(hydroxymethyl)-acrylamide hydrogel to introduce hydrophobic cores. In this work we have focussed to improve the sustainable drug release and toxic dye removal performance of hydrogel by introducing β–cyclodextrin (β-CD). Four different grades of β-cyclodextrin grafted acrylamide-*co*-N-(hydroxymethyl)-acrylamide have been synthesized via free radical polymerization technique at room temperature. Different proportions of β-CD and fixed amount of acrylamide (AM), N-(Hydroxymethyl)-acrylamide (NHMA) and 2,2' –Azobis-[2-(2-imidazolin-2-yl)-propane] dihydrochloride (AIPD as an Initiator) have been used. The synthesized grades were characterized by using FT-IR, SEM, TGA, UV-Visible

and powder XRD. Hydrogels have showed high swelling capacity i.e. 3000 times higher than dry weight. The diffusion studies of drug loaded hydrogels have been performed and it follows quasi-fickian drug release behaviour. Cumulative drug release studies of Diclofenac Sodium has been investigated in buffer solution at pH 7.4 for 66 hrs and toxic cationic dye (Methylene Blue) removal studies have been done in highly concentrated dye contaminated aqueous solution at neutral pH. Hydrogel results in complete removal of MB dye with lesser dose and in short span of time. β-cyclodextrin grafted acrylamide-*co*-N-(hydroxymethyl)-acrylamide-2 and β-cyclodextrin grafted acrylamide-*co*-N-(hydroxymethyl)-acrylamide-3 shows highest 77 % drug release and almost 100 % dye removal from solution respectively.



Scheme 5: Schematic representation of multiple applications of β-CD based hydrogel in dye removal and drug delivery systems.

Chapter eight: "Conclusions"

The conclusion of thesis has been obtained from the different chapters which consists the wide investigation of synthesis of different series of polymers, characterizations and their applications.